Incommensurate magnetic order in Ag_2NiO_2

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The nature of the magnetic transition of the half-filled triangular antiferromagnet Ag_2NiO_2 with T_N=56K was studied with positive muon-spin-rotation and relaxation (μ^+SR) spectroscopy. Zero field μ^+SR measurements indicate the existence of a static internal magnetic field at temperatures below T_N. Two components with slightly different precession frequencies and wide internal-field distributions suggest the formation of an incommensurate antiferromagnetic order below 56 K. This implies that the antifrerromagnetic interaction is predominant in the NiO_2 plane in contrast to the case of the related compound $NaNiO_2$. An additional transition was found at ~22 K by both μ^+SR and susceptibility measurements. It was also clarified that the transition at ~260 K observed in the susceptibility of Ag_2NiO_2 is induced by a purely structural transition.

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I. INTRODUCTION

Two-dimensional triangular lattice (2DTL) antiferromagnets with a half-filled (e_g) state exhibit a variety of magnetically ordered states due to competition between the antiferromagnetic (AF) interaction and geometrical frustration. The discovery of superconductivity in $Na_{0.35}CoO_2$∗$1.3H_2O$ [1] leads to an additional interest in the possible relationship between magnetic and superconducting order parameters in the 2DTL near half-filling. The layered nickel dioxides, a series of materials with chemical formula $A^+Ni^{3+}O_2$, such as rhombohedral $LiNiO_2$,[2, 3], $NaNiO_2$[4, 5, 6], and $AgNiO_2$,[7, 8] in which Ni ions form the 2DTL by the connection of edge-sharing NiO_6 octahedra, has been considered to be good candidates for an ideal half-filled 2DTL. In these materials at low temperature, there is a strong interaction between the Ni^{3+} ions and the crystalline electric field of the NiO_6 octahedron. This causes the Ni^{3+} ions to be in the low spin state with a $t_{2g}^6 e_g^1$ (S=1/2) configuration.

Among the three layered nickel dioxides, $NaNiO_2$ is perhaps the best investigated. It exhibits two transitions at T_{JT} ~480 K and T_N=23 K. The former is a cooperative Jahn-Teller (JT) transition from a high-T rhombohedral phase to a low-T monoclinic phase, while the latter is a transition into an A-type AF phase — i.e. ferromagnetic (FM) order in the NiO_2 plane but AF between the two adjacent NiO_2 planes, as has been reconfirmed very recently by both neutron diffraction[4, 5] and positive muon spin rotation/relaxation (μ^+SR) experiments.[6] The magnetic order is associated with the JT induced trigonal distortion which stabilizes a half occupied d_{z^2} orbital.[9]

Although $LiNiO_2$ and $NaNiO_2$ are structurally very similar, $LiNiO_2$ shows dramatically different magnetic properties. $LiNiO_2$ exhibits neither a cooperative JT transition nor long-range magnetic order down to the lowest T investigated. In fact, both heat capacity and NMR measurements suggest a spin-liquid state with short-range FM correlations.[2] Chatterji *et al.*[3], however, found a rapid increase in the muon spin relaxation rates in $LiNiO_2$ below ~10 K using the longitudinal field-μ^+SR technique, suggesting a spin-glass-like behavior below 10 K. The discrepancy between the two results is considered to be a sample-dependent phenomenon that arises from the difficulties in preparing stoichiometric $LiNiO_2$. The third compound, $AgNiO_2$, also lacks a cooperative JT transition. A magnetic transition T_N was clearly observed by both susceptibility (χ) and μ^+SR measurements but long-range magnetic order was not detected by a neutron diffraction experiment even at 1.4 K.[8]

While the nature of the magnetic ground states of $LiNiO_2$ and $AgNiO_2$ is still not clear, the FM interaction on the 2DTL NiO_2 plane has been thought to be common for all the layered Ni dioxides with a half-filled state because of the clear magnetic order observed in $NaNiO_2$. In this paper, we present measurements that demonstrate this supposition is incorrect. This is accomplished by investigating the magnetism in Ag_2NiO_2, a material that can be represented by the chemical formula $(Ag_2)^+Ni^{3+}O_2$ and hence is expected to have a NiO_2 plane that has properties identical to the above three layered nickel dioxides. However, in Ag_2NiO_2, static AF order, likely the formation of an incommensurate AF struc-

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ture in the NiO_2 plane, is observed instead.

Disilver nickel dioxide Ag_2NiO_2 is a rhombohedral system with space group $R\overline{3}m$ (a_H = 0.29193 nm and c_H = 2.4031 nm for the hexagonal unit-cell) [10] that was found to exhibit two transitions at T_S=260 K and T_N=56 K by resistivity and χ measurements, while the symmetry remains rhombohedral down to 5 K.[11] Interestingly, Ag_2NiO_2 shows metallic conductivity down to 2 K probably due to a quarter-filled Ag 5s band, as in the case of Ag_2F.[12] Very recently, Yoshida *et al.* proposed the significance of the AF interaction in the 2DTL NiO_2 plane from the $\chi(T)$ measurement.[11]

II. EXPERIMENTAL

A powder sample of Ag_2NiO_2 was prepared at the ISSP of the University of Tokyo by a solid-state reaction technique using reagent grade Ag_2O and NiO powders as starting materials. A mixture of Ag_2O and NiO was heated at 550°C for 24 h in oxygen under a pressure of 70 MPa. A more detailed description of the preparation and characterization of the powder is presented in Ref. 11.

Susceptibility (χ) was measured using a superconducting quantum interference device (SQUID) magnetometer (mpms, Quantum Design) in the temperature range between 400 and 5 K under magnetic field $H \leq 55$ kOe. For the μ^+SR experiments, the powder was pressed into a disk of about 20 mm diameter and thickness 1 mm, and subsequently placed in a muon-veto sample holder. The μ^+SR spectra were measured on the M20 surface muon beam line at TRIUMF. The experimental setup and techniques were described elsewhere.[13]

III. RESULTS AND DISCUSSION

A. Below T_N

Figure 1 shows zero-field (ZF-)μ^+SR time spectra in the T range between 1.9 K and 60 K for a powder sample of Ag_2NiO_2. A clear oscillation due to quasi-static internal fields $\boldsymbol{H}_{\rm int}$ is observed below 54 K, unambiguously establishing the existence of long-range magnetic order in the sample. Interestingly, as T is decreased from 60 K, the relaxation rate first decreases down to ~20 K and then *increases* as T is lowered further. By contrast, the average oscillation frequency increases monotonically down to 1.9 K. This implies that the distribution of $\boldsymbol{H}_{\rm int}$ at $T \geq 54$ K and ≤ 20 K is larger than that at 20 K< T <54 K.

This is further established by the T dependence of the Fourier Transform of the ZF-μ^+SR time spectrum shown in Fig. 2. Note that there is clearly line broadening below 20 K as well as above 54 K. The line-broadening above 54 K is reasonably explained by critical phenomena in the vicinity of T_N=56 K; however, it is difficult to understand the origin of the line-broadening below 20 K using a classical AF model without invoking the presence of an additional magnetic transition. Furthermore, even the spectrum at 30 K, which is the sharpest FFT measured, consists of a main peak at ~14 MHz and a shoulder around 16 MHz, suggesting a wide distribution of $\boldsymbol{H}_{\rm int}$ in Ag_2NiO_2.

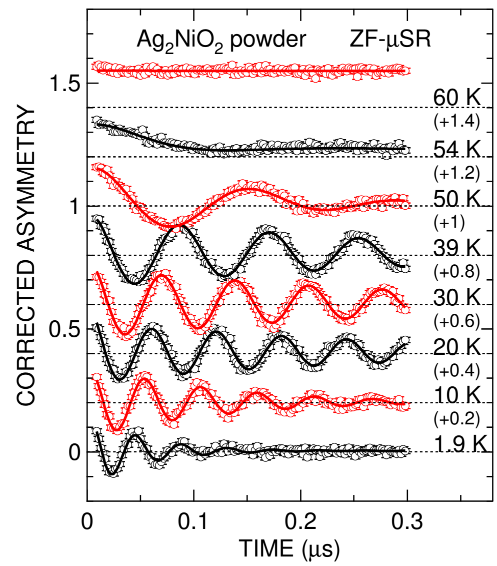

FIG. 1: (Color online) Temperature dependence of the ZF-μ^+SR time spectra of a powder sample of Ag_2NiO_2. Each spectrum is offset by 0.2 for clarity of the display. The solid lines represent the fitting result using Eq. (1).

We therefore use a combination of three signals to fit the ZF-μ^+SR time spectrum:

$$\begin{aligned} A_0\,P_{\rm ZF}(t) \;=\; & A_1\,\cos(\omega_{\mu,1}t+\phi)\,\exp(-\lambda_1 t) \\ +\; & A_2\,J_0(\omega_{\mu,2}t)\,\exp(-\lambda_2 t) \\ +\; & A_{\rm slow}\,\exp(-\lambda_{\rm slow}t), \end{aligned} \tag{1}$$

where A_0 is the empirical maximum muon decay asymmetry, A_1, A_2 and $A_{\rm slow}$ are the asymmetries associated with the three signals, $J_0(\omega_{\mu,2}t)$ is a zeroth-order Bessel function of the first kind that describes the muon polarization evolution in an incommensurate spin density wave (IC-SDW) field distribution,[13] and $\omega_{\mu,1} < \omega_{\mu,2}$.

Although $J_0(\omega t)$ is widely used for fitting the ZF-μ^+SR spectrum in an IC-SDW state, it should be noted that $J_0(\omega t)$ only provides an approximation of the generic IC magnetic field distribution. This is because the lattice sum calculation of the dipole field at the muon site ($\boldsymbol{H}_{\rm IC}$) due to an IC magnetic structure lies in a plane and traces out an ellipse. The half length of the major axis of the ellipse corresponds to $H_{\rm max}$, whereas half of the minor axis corresponds to $H_{\rm min}$. As a result, the IC magnetic

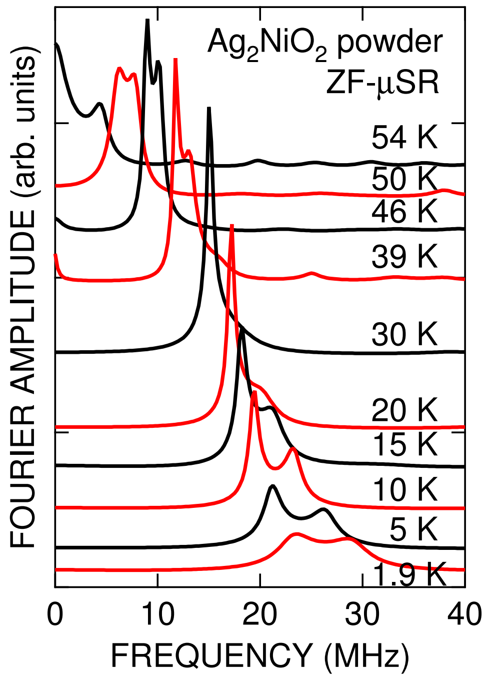

FIG. 2: (Color online) Temperature dependence of the Fourier Transform of the ZF-μ^+SR time spectrum for Ag_2NiO_2.

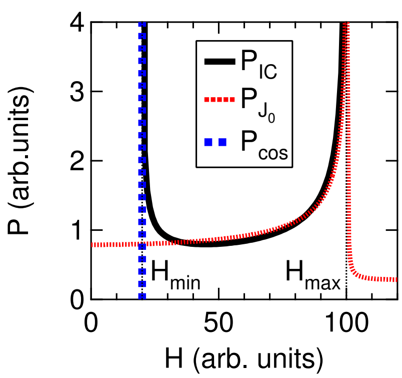

FIG. 3: (Color online) The distribution of the magnitude of the magnetic field H due to a generic incommensurate magnetic structure described in the text. The distribution corresponding to a Bessel function $J_0(\omega_2 t)$ and a $\cos(\omega_1 t)$ are also plotted for comparison. Here, $\gamma_\mu H_{\rm max} = \omega_2$ and $\gamma_\mu H_{\rm min} = \omega_1$.

field distribution $P_{\rm IC}$ is generally given by;

$$P_{\rm IC} = P(\boldsymbol{H}_{\rm IC}) = \frac{2}{\pi}\frac{H}{\sqrt{(H^2 - H^2_{\rm min})(H^2_{\rm max} - H^2)}}. \quad (2)$$

The distribution diverges as H approaches either $H_{\rm min}$ or $H_{\rm max}$ (see Fig. 3). $J_0(\omega t)$ describes the field distribution very well except in the vicinity of $H_{\rm min}$, and the value of ω should be interpreted as an accurate measure of $H_{\rm max}$. However, $J_0(\omega t)$ provides no information on $H_{\rm min}$. Hence, the first term $A_1\cos(\omega_{\mu,1}t + \phi_1)\exp(-\lambda_1 t)$ is added in Eq. (1) to account for the intensity around $H_{\rm min}$ and to determine the value of $H_{\rm min}(=\omega_{\mu,1}/\gamma_\mu)$ [15] (γ_μ is the muon gyromagnetic ratio and $\gamma_\mu/2\pi$=13.55342 kHz/Oe). In other words, only when $H_{\rm min}$=0, Eq. (2) is well approximated by $J_0(\omega t)$. Here it should be emphasized that μ^+SR spectra are often fitted in a time domain, i.e. not by Eq. (2) but by Eq. (1), since information on all the parameters such as A, ω, λ and ϕ are necessary to discuss the magnetic nature of the sample.

We note that the data can also be well-described using two cosine oscillation signals, $A_1\cos(\omega_{\mu,1}t + \phi_1)\exp(-\lambda_1 t) + A_2\cos(\omega_{\mu,2}t + \phi_2)\exp(-\lambda_2 t)$ with ϕ_2=-54$\pm$10$^{\rm o}$ below $T_{\rm N}$. The delay is physically meaningless, implying that the field distribution fitted by a cosine oscillation, i.e. a commensurate $\boldsymbol{H}_{\rm int}$ does not exist in Ag_2NiO_2.[13] Furthermore, as T decreases from 54 K, A_1 (A_2) decreases (increases) linearly with T from 0.15 (0) at 54 K to 0 (0.15) at 1.9 K. In order to explain the $A_1(T)$ and $A_2(T)$ curves, one would need to invoke the existence of two muon sites, and a situation whereby the population of μ^+ at each site is changing in proportion to T. Such behavior is very unlikely to occur at low T. Hence, we believe that our data strongly suggests the appearance of an IC-AF order in Ag_2NiO_2 below $T_{\rm N}$, as predicted by the calculation using a Mott-Hubbard model (discussed later). Such a conclusion is also consistent with the fact that the paramagnetic Curie temperature is -33 K estimated from the $\chi(T)$ curve below 260 K.[11]

Figures 4(a) - 4(d) show the T dependence of the muon precession frequencies (ν_i=$\omega_{\mu,i}/2\pi$), the volume fraction of the paramagnetic phases ($V_{\rm para}$), $\Delta\nu = \nu_2 - \nu_1$, λ_1, λ_2, the asymmetries A_1+A_2, A_1, A_2, $A_{\rm slow}$, and χ for the powder sample of Ag_2NiO_2. Here, $V_{\rm para}$ is estimated from the weak transverse field (wTF-) μ^+SR experiment described later. In agreement with the FFTs shown in Fig. 3, as T is decreased from 60 K, ν_2 appears at 54 K. It then increases monotonically with decreasing T down to around 20 K, and then increases more rapidly upon further cooling. The $\nu_1(T)$ curve exhibits a similar behavior to that observed for $\nu_2(T)$. It is noteworthy that as T is decreased from 80 K, the $V_{\rm para}(T)$ curve shows a sudden drop down to $\sim$ 0 at $T_{\rm N}$, indicating that the whole sample enters into an IC-AF state.

As T decreases from $T_{\rm N}$, $\Delta\nu$, which measures the distribution of $\boldsymbol{H}_{\rm int}$ in the IC-AF phase, rapidly decreases down to $\sim$0.8 MHz at 40 K, then seems to level off the lowest value down to $\sim$20 K and then increases with increasing slope ($|{\rm d}\Delta\nu/{\rm d}T\ |$) until it reaches 4 MHz at 1.9 K. The overall T dependence of $\Delta\nu$ is similar to that of λ_i. This behavior is expected since a large $\Delta\nu$ naturally implies a more inhomogeneous field distribution—i.e, an increased flattening of the ellipse that enhances λ_i. The asymmetry of the IC magnetic phase, A_1+A_2, also increases monotonically with decreasing T, although

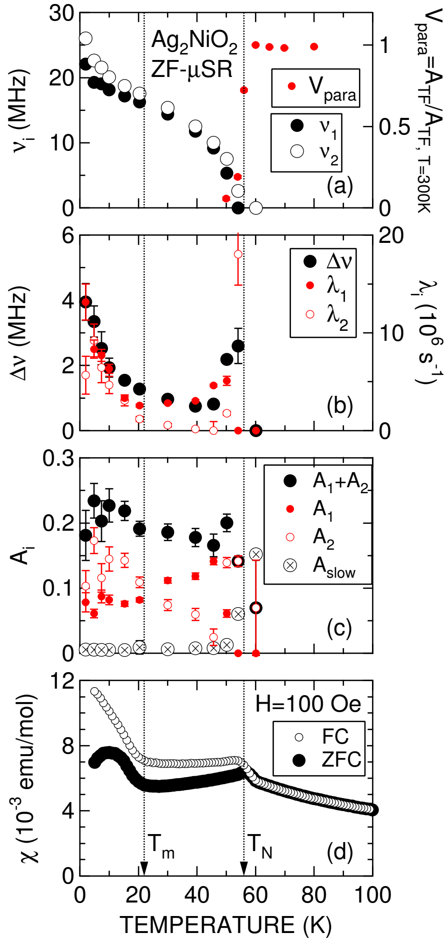

FIG. 4: (Color online) Temperature dependences of (a) the muon precession frequencies (ν_i=$\omega_{\mu,i}/2\pi$) and normalized transverse field asymmetry that roughly corresponds to the volume fraction of the paramagnetic phases in the sample ($V_{\rm para}$), (b) $\Delta\nu = \nu_2 - \nu_1$, λ_1 and λ_2, (c) the asymmetries A_1+A_2, A_1, A_2 and $A_{\rm slow}$ and (d) χ for the powder sample of Ag_2NiO_2. χ was measured in zero-field-cooling ZFC and field-cooling FC mode with H = 100 Oe.

a small jump likely exists around 20 K. The existence of a significant A_1 underscores the inappropriateness of fitting the ZF-μ^+SR data with only a $J_0(\omega_{\mu,2}t)$ term. In fact, note that $A_1 < A_2$ above 20 K, suggesting that the IC-AF order develops/completes below 20 K. This is consistent with the rapid increases in $\Delta\nu$ and λ_i below 20 K, as described above.

The behavior of the muon parameters is quite consistent with the $\chi(T)$ curve, which exhibits a sudden increase in the slope ($|{\rm d}\chi_{\rm FC}/{\rm d}T\ |$) below ∼22 K(=$T_{\rm m}$) with decreasing T. Note the $\chi(T)$ curve measured under ZFC conditions starts to deviate from that measured in the FC configuration below $T_{\rm N}$, suggesting the development of a ferro- or ferrimagnetic component probably due to a canted spin structure.[5] The ferro- or ferrimagnetic behavior is however observed only at low H, although

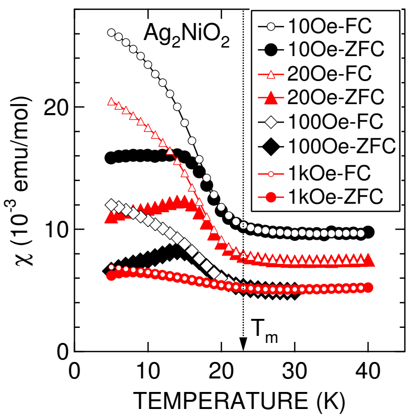

FIG. 5: (Color online) Temperature dependence of χ measured in both ZFC and FC mode well below $T_{\rm N}$ = 56 K with H=10 Oe, 20 Oe, 100 Oe and 1 kOe for Ag_2NiO_2.

the cusp at $T_{\rm N}$ is clearly seen with H=100 - 10 kOe (see Figs. 4(d) and 6(d)). Below $T_{\rm m}$, $\chi_{\rm FC}$ increases with decreasing T, while the slope is suppressed by increasing H (see Fig. 5). Keeping in mind that μ^+SR is insensitive to magnetic impurities, we conclude that Ag_2NiO_2 undergoes a transition from a paramagnetic to an IC-AF state at $T_{\rm N}$=56 K and then to a slightly different ordered state at $T_{\rm m}$ ∼22 K.

It is worth contrasting the current μ^+SR results on Ag_2NiO_2 with those in related compounds $NaNiO_2$ and $AgNiO_2$. The ZF-μ^+SR spectrum on a powder sample of $NaNiO_2$ consists of two signals below $T_{\rm N}$(∼20 K): an exponentially relaxing cosine oscillating signal (same as the first term in Eq. (1)) as the predominant component and a minor signal described by an exponential relaxation.[6] This indicates that the whole $NaNiO_2$ sample enters into a commensurate AF state below $T_{\rm N}$, being consistent with the magnetic structure determined by neutron diffraction experiments, i.e., an A-type AF order.[4, 5] Interestingly, the value of $\nu_{\rm T\to 0\ K}$=64.2 MHz, which corresponds to $H_{\rm int}$ ∼0.5 T, is 2.5 times higher than that for Ag_2NiO_2. The muon site in $NaNiO_2$ is assigned to the vicinity of the O ions,[6] and is thought to be also reasonable for the other layered nickel dioxides. The differences between the μ^+SR results on $NaNiO_2$ and Ag_2NiO_2 hence suggest that the magnetic structure of Ag_2NiO_2 is most unlikely to be an A-type AF. Furthermore, there are no indications for additional transitions of $NaNiO_2$ below $T_{\rm N}$ by χ, μ^+SR and neutron diffraction measurements.[4, 5, 6]

In $AgNiO_2$, the primary ZF-μ^+SR signal is one that exponentially relaxes down to the lowest T (∼3 K). Below $T_{\rm N}$(=28 K), three minor oscillating components appear. These have small amplitudes and correspond to internal fields from 0.2 to 0.33 T (27 - 45 MHz).[8] The comparison between $AgNiO_2$ and Ag_2NiO_2 indicates that the interlayer separation ($d_{\rm NiO_2}$) enhances the static magnetic order in the NiO_2 plane. It is highly unlikely that the AF

interaction through the double Ag_2 layer is stronger than that through the single Ag layer, since $d_{\mathrm{NiO_2}}$=0.801 nm for Ag_2NiO_2[10] and 0.612 nm for $AgNiO_2$.[7]

Our results therefore suggest that the AF order exists in the NiO_2 plane, in contrast to the situation in $NaNiO_2$. Assuming the AF interaction is in the NiO_2 plane, an IC-spiral SDW phase is theoretically predicted to appear in a half-filled 2DTL[16] (calculated using the Hubbard model within a mean field approximation with $U/t \geq$ 3.97, where U is the Hubbard on-site repulsion and t is the nearest-neighbor hopping amplitude). In order to further establish the magnetism in Ag_2NiO_2, it would be interesting to carry out neutron diffraction experiments to determine the magnetic structure below T_{N} and below T_{m}.

We wish here to mention that if the valence state of the Ni ion in the NiO_2 plane can be varied for Ag_2NiO_2, the resultant phase diagram should serve as an interesting comparison with that of A_xCoO_2 (A=alkali elements) with x ≤0.5. Unlike Li_xNiO_2, (Ag_2)-deficient samples are currently unavailable, probably because of the metal-like Ag-Ag bond in the disilver layer.[10] A partial substitution for Ag_2 by other cations has thus far also been unsuccessful for reasons unknown.

B. Near T_{S}

In order to elucidate the magnetic behavior above T_{N}, in particular near T_{S}=260 K, we carried out weak transverse field (wTF-) μ^+SR measurements up to 300 K. The wTF-μ^+SR spectrum was fitted by a combination of a slowly and a fast relaxing precessing signal; the former is due to the external field and the latter due to the internal AF field (same as the first term in Eq. (1));

$$\begin{aligned} A_0\,P_{\mathrm{TF}}(t) &= A_{\mathrm{TF}}\cos(\omega_{\mu,\mathrm{TF}}t+\phi_{\mathrm{TF}})\exp(-\lambda_{\mathrm{TF}}t) \\ &+ A_{\mathrm{AF}}\cos(\omega_{\mu,\mathrm{AF}}t+\phi_{\mathrm{AF}})\exp(-\lambda_{\mathrm{AF}}t), \end{aligned} \quad (3)$$

where $\omega_{\mu,\mathrm{TF}}$ and $\omega_{\mu,\mathrm{AF}}$ are the muon Larmor frequencies corresponding to the applied weak transverse field and the internal AF field, ϕ_{TF} and ϕ_{AF} are the initial phases of the two precessing signals and A_n and λ_n (n = TF and AF) are the asymmetries and exponential relaxation rates of the two signals. Note that we have ignored the $J_0(\omega t)$ term in Eq. (3) since we are primarily interested in the magnetic behavior above T_{N}.

The results are shown in Fig. 6 together with χ^{-1}. Besides the transition at 56 K, there are no anomalies up to 300 K in the normalized asymmetries, the relaxation rate (λ_{TF}) or the shift of the muon precession frequency ($\Delta\omega_{\mu,\mathrm{TF}}$). Transverse field (TF-) μ^+SR measurements at H=2600 Oe, which should be about 50 times more sensitive to frequency shifts than the wTF measurements, show no obvious changes in $\Delta\omega_{\mu,\mathrm{TF}}$ at T_{S} either. On the other hand, the $\chi^{-1}(T)$ curve exhibits a clear change in slope at T_{S}. Above 60 K, the normalized wTF-asymmetry (A_{TF}) levels off to its maximum value — i.e. the sample volume is almost 100% paramagnetic. This

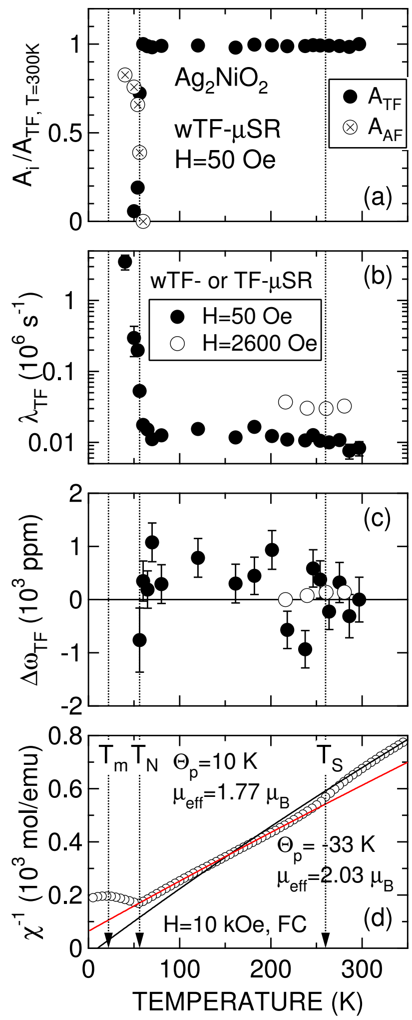

FIG. 6: (Color online) Temperature dependences of (a) the normalized A_{TF} and A_{AF}, (b) λ_{TF}, (c) the shift of the muon precession frequency, $\Delta\omega_{\mu,\mathrm{TF}}$ and (d) the inverse susceptibility, χ^{-1} in the Ag_2NiO_2 powder. The wTF and TF data were obtained by fitting using Eq. (3). χ was measured in FC mode with H=10 kOe. The paramagnetic Curie temperature (Θ_{p}) and the effective magnetic moment of Ni ions (μ_{eff}) are calculated above and below T_{S} by the Curie-Weiss law in the general form; $\chi = C(T-\Theta_{\mathrm{p}})^{-1} + \chi_0$.

therefore suggests that T_{S} is induced by a purely structural transition and there is no dramatic change in the spin state of Ni ions; that is, T_{S} is unlikely to be a cooperative JT transition. This is consistent with the fact that the crystal structure remains rhombohedral down to 5 K.[11]

IV. SUMMARY

Positive muon spin rotation/relaxation (μ^+SR) spectroscopy has been used to investigate the magnetic prop-

erties of a powder sample of Ag_2NiO_2 in the temperature range between 1.9 and 300 K. Zero field μSR measurements suggest the existence of an incommensurate antiferromagnetic (AF) order below T_N=56 K. An additional transition was also found at T_m=22 K by both μ^+SR and susceptibility measurements.

The current results, when compared to the results in $AgNiO_2$, indicate that magnetism in the half-filled 2DTL of the NiO_2 plane is strongly affected by the interlayer distance. In other words, the ground state of the half-filled NiO_2 plane is not a ferromagnetic (FM) ordered state or an FM spin-liquid or spin-glass, but is instead an AF frustrated system. The FM behavior in $NaNiO_2$ is therefore thought to be induced by a Jahn-Teller induced trigonal distortion.

Acknowledgments

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